DISCOVERY

Diffusing Species into Some Host Metals in Semi-infinite Cylindrical Solids

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General Note
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ABSTRACT

Diffusing species into some host metals in semi-infinite cylindrical solids and key thermodynamic properties were examined. The governing Bessel's differential equation of order zero and time dependent first order differential equation were obtained. Analytical solutions showed that stable concentration of the system and partition function was achieved as the temperature increases. However, the thermodynamic function of Helmholtz free energy is enhanced as the radius of the diffusing species into the host metals at a fractional exponent of 0.6 is increased and the reverse was observed with the entropy of the system while the internal energy and specific heat are independent of the diffusing species parameters. A mathematical model was also proposed to calculate the diffusion coefficients of the diffusing species into the host metals by adjustment of the constant in the model.

Keywords: Diffusion, Host Metals, Cylindrical Solids, Model, Partition Function

1. INTRODUCTION

Diffusion is regarded as the stepwise movement of atoms from lattice site to lattice site. It can also be viewed as the process of mixing which involves the migration of atoms from region of higher concentration to that of lower concentration or the shifting of atoms and molecules to new areas within a given material resulting in the uniformity of composition as a result of thermal agitation (Rajput2013). Diffusion is fundamentally statistical physics in nature and the process irreversible hence increases entropy. It is also synonymous with phase change and movement is short-range. Diffusion in solids is a slow process and its rate increases with increase in temperature which is vital in metallurgical processes. As a result of the applications of diffusion which include phase changes, metal bonding, oxidation of metals, doping of semiconductors, recovery and recrystalization and a host of researches are abounded. Hung *et al*. (2000), in the study of self-diffusion in metals using the fourth order moment approximation, deduced the activation energy and pre-exponential values for some metals at high and low temperature regimes which are in good agreement with experimental results. Martinez-Vera *et al*. (2015), examined the diffusion co-efficient estimation in shrinking solids and presented an experimental results of the drying kinetics for a solid that shrinks in volume during the drying process depending on the drying temperature. Povstenko *et al*. (2017) tackled fractional diffusion in a solid with mass absorption wherein, a model was used to illustrate far reaching results. Carballido *et al*. (2011), proposed a turbulent diffusion of large solids in a protoplanetary disc with two models to predict the same radial turbulent diffusion coefficient for small particles. Duda *et al*. (2007), in the study of modeling of coupled deformation- diffusion – damages in elastic solids, used numerical algorithm to solve the discrete system of equations for the application of the hydrogen embrittlement. In the study of volumes of activation for diffusion in solids, Reyes (1958), critically assessed the activation volumes of some simple models of lattice defects and compared with experimental measurements. The comparison was satisfactory in many cases. A general mathematical approach to the rigorous treatment of experimental data on non stationary state diffusion in solids of complex shape was developed by Beeker (1959) in the study of diffusion in solids of arbitrary shape with application to the drying of the wheat kernel. A new theoretical approach was established by Nguyen (2018) to define transport coefficients of charge and mass transport in porous material directly from impedance data in a study of new approach to determine gas diffusion coefficient in porous solids by Electrochemical Impedance Spectroscopy (EIS): Application for NH_3 and CO_2 absorption Zircomia and Zeolite type 5A. In the study of measurement of solids diffusion coefficient by a temperature programmed method, Kapoor and Oyama, (2011), presented a method for determining diffusivities in solids where the diffusing species absorbs or reacts at the external surfaces and where the diffusivity does not vary appreciably with concentration. The method requires measuring the flux of the diffusive species out of the solids under the influence of temperature program. A model is proposed based on isothermal Fickian diffusion. Korblein et al (1985), examined the diffusion process in solid Li –Mg and Li – Ag alloys and the spin-lattice relaxation of ^{8}Li and opined that Ag is found to diffuse faster than Li. Experimental results displaying the quantum diffusion in different systems was the plank of the study of quantum diffusion in solids by Kagan (1992). In a study of sucrose diffusion in aqueous solution, Price et al (2016), reported measured sucrose diffusion coefficient using Stokes-Einstein equation and claimed it fits well with experimental data. A recent study of transfer phenomena in fluid and heat flows VIII by Kolisnychenko (2019) highlighted a compilation of theoretical and practical aspects of modeling and numerical investigation of diffusion convection and MHD mixed convection flows. The main aim of this study is to consider temperature and concentration dependent systems of diffusion coefficient and highlight some of its thermodynamic properties in semi-infinite cylindrical solids.

2. FORMALISM

The governing partial differential equation of a long circular cylinder in which diffusion is everywhere radial, concentration C is therefore a function of radius r and time t and the model becomes

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial C}{\partial r}\right) \qquad (1)$$

with the boundary conditions

$$C(1,t) = C_1$$
$$C(2,t) = C_2 \qquad (2)$$
$$C(r,0) = C_0$$

The diffusion coefficient D (concentration- dependent system) is given by

$$D = D_s e^{\beta_1 C}$$

(3)

where D_s is the diffusion coefficient for the surface concentration of the solids and β_1 is a constant.

The diffusion coefficient in a temperature-dependent systems obey the Arrhenius-type equation

$$D = D_0 e^{-\frac{E_a}{RT}}$$

(4)

where E_a, R, T and D_0 are respectively the activation energy, universal gas constant, temperature and pre-exponential factor.

A generalized expression for the activation energy according to Atkins and Paula (2006) is given as

$$E_a = RT^2 \left(\frac{d \ln D}{dT} \right)$$

(5)

which incorporate the quantum mechanical tunneling role in the diffusion of the reacting metals.

According to Price et al (2016), the Fractional Stokes-Einstein relation for diffusion constant rate is given as

$$D = \frac{k_B T}{6 \pi \mu r^\varepsilon}$$

(6)

where $\varepsilon < 1$ and ranges from $0.6 - 0.9$, μ is viscosity and k_B is Boltzmann constant.

To determine the activation energy of the system, equation (6) is put into equation (5) and the result is given as

$$E_a = RT = N_A k_B T$$

(7)

where N_A is Avogadro's constant.

The quantity of diffusing substance Q_t which diffuses through unit length of a cylinder in time t is given by Crank (1975) as

$$Q_t = \frac{2\pi Dt (C_2 - C_1)}{\ln(2)}$$

(8)

If Q_t is measured in a concentration - dependent system, the mean value of the diffusion coefficient from equation (8) is given as

$$\frac{\int_{C_1}^{C_2} D dc}{(C_2 - C_1)}$$

(9)

Method of solution

To solve equation (1), separating the variables techniques is assumed, which is of the form

$$C(r,t) = R(r)T(t) \tag{10}$$

Equation (10) is put into equation (1) and the resulting expression is equated to a constant $-\beta^2$, two equations result. They are

$$T'(t) + \beta^2 DT(t) = 0 \tag{11}$$

$$R''(r) + \frac{1}{r}R'(r) + R(r)\beta^2 = 0 \tag{12}$$

Using the method of variable separable for equation (11) and the Frobenius method of the form $R(r) = \sum_{n=0}^{\infty} a_n r^{n+a}$ for equation (12) and substituting the resulting equations into equation (10), the result is given as

$$C(r,t) = \left[a_0\left(1 + \frac{\beta^2 r^2}{4} + \frac{\beta^4 r^4}{64} + ...\right) + a_1\left(r + \frac{\beta^2 r^3}{9} + \frac{\beta^4 r^5}{225} + ...\right) \right]\left(e^{-\beta^2 Dt}\right) \tag{13}$$

where the constant of equation (11) has been absorbed into a_0 and a_1.

Imposing the boundary conditions and solving the resulting simultaneous equations, the values of $a_0 = \dfrac{C_1\alpha_1\alpha_4 - \alpha_2^2 C_2}{\alpha_1}$ and

$$a_1 = \frac{C_2\alpha_2 - \alpha_3 C_1}{\alpha_1\alpha_4 - \alpha_2\alpha_3}$$

where $\alpha_1 = \left[\left(1 + \dfrac{\beta^2}{4} + \dfrac{\beta^4}{64} + ...\right)\right]\left(e^{-\beta^2 Dt}\right)$

$$\alpha_2 = \left[\left(1 + \frac{\beta^2}{9} + \frac{\beta^4}{225} + ...\right)\right]\left(e^{-\beta^2 Dt}\right)$$

$$\alpha_3 = \left[\left(1 + \frac{4\beta^2}{4} + \frac{16\beta^4}{64} + ...\right)\right]\left(e^{-\beta^2 Dt}\right)$$

$$\alpha_4 = \left[\left(2 + \frac{8\beta^2}{9} + \frac{32\beta^4}{225} + ...\right)\right]\left(e^{-\beta^2 Dt}\right)$$

To determine the concentration from the concentration-dependent diffusion coefficient, equation (3) is equated to equation (6) and the expression takes the form

$$C = \frac{1}{\beta_1}\ln\left(\frac{k_B T}{D_s 6\pi\mu r^\varepsilon}\right) \tag{14}$$

Following Atkins and Paula (2006), equation (6) is put into equation (3), the expression is put into equation (4) and finally into equation (5), the diffusion coefficient takes the form

$$D = Exp\frac{T^2}{2}\ln\left(\frac{k_B T}{D_s 6\pi\mu r^\varepsilon}\right) - \frac{T^2}{4} \tag{15}$$

where the constant of integration is assumed unity

3. THERMODYNAMIC FUNCTIONS

It has been stated earlier in the introduction that diffusion is statistical physics in nature, therefore to determine the thermodynamic properties of the diffusing species into host metals cannot be overemphasized. Any physical system with thermodynamic properties, needed the introduction of the concept of partition function given by the expression

$$Z_n(T) = \sum_{n=0}^{\infty} Exp - \left(\frac{E_n}{k_B T} \right) \tag{16}$$

where E_n is energy.

Equating equations (4) and (6), the expression takes the form

$$E_a = -RT \ln \left(\frac{k_B T}{D_o 6\pi\eta r^\varepsilon} \right) \tag{17}$$

Assuming the activation energy to be the energy of the partition function, equation (16) takes the form

$$Z_n(T) = \sum_{n=1}^{\infty} Exp N_A \ln \left(\frac{k_B T}{D_o 6\pi\eta r^\varepsilon} \right) \tag{18}$$

Thermodynamic functions such as Helmholtz Free Energy F(T), Entropy S(T). Internal Energy U(T) and Specific Heat $C_v(T)$ are obtained from the Partition function as follows

$$F(T) = -\frac{1}{T} \ln Z(T) \tag{19}$$

$$S(T) = -k_B \frac{\partial F(T)}{\partial T} \tag{20}$$

$$U(T) = -\frac{\partial}{\partial T} \ln Z(T) \tag{21}$$

$$C_v(T) = k_B \frac{\partial U(T)}{\partial T} \tag{22}$$

Values of constants and other parameters used

$$k_B = 1.38065 x 10^{-23} J / k$$
$$N_A = 6.02214 x 10^{23} mol^{-1}$$
$$R = 8.31447 J / kmol$$
$$C_1 = 1 kg / mol$$
$$C_2 = 2 kg / mol$$
$$\varepsilon = 0.6$$

Table 1:   Diffusion Data (Rajput, 2003; Hilderbrand and Lamoreaux, 1976)

Diffusing Species	Viscosities $\eta(Ns / m^2)$	Host Metals	Pre-exponential Factor $D_0 \; (m^2 / s)$	Activation Energy k/mole	Diffusion coefficient D (m^2 / s)
Copper (Cu)	0.44	Cu	$7.8x10^{-5}$	211	$4.2x10^{-19}$
Zinc (Zn)	0.18	Cu	$2.4x10^{-5}$	189	$4.0x10^{-18}$
Aluminium(Al)	0.09	Al	$2.3x10^{-4}$	144	$4.2x10^{-14}$
Copper (Cu)	0.44	Al	$1.2x10^{-4}$	131	$4.0x10^{-14}$
Copper (Cu)	0.44	Nickel(Ni)	$2.7x10^{-5}$	256	$1.3x10^{-22}$

Table 2: Calculated values of diffusion parameters

Diffusing Species-Host Metals	Concentration $C(kg / s)$	Constant $\beta_1 \; (mol / kg)$	Diffusion coefficient $D\,(m^2 / s)$
Cu-Cu	-38.6433	0.850	$4.2354 \, x10^{-19}$
Zn-Cu	-36.5709	0.803	$4.23186 \, x10^{-18}$
Al-Al	-38.1377	0.588	$4.19458 \, x10^{-14}$
Cu-Ni	-37.5828	1.061	$1.29974 \, x10^{-22}$
Cu-Al	-38.4610	0.551	$4.06762 \, x10^{-14}$
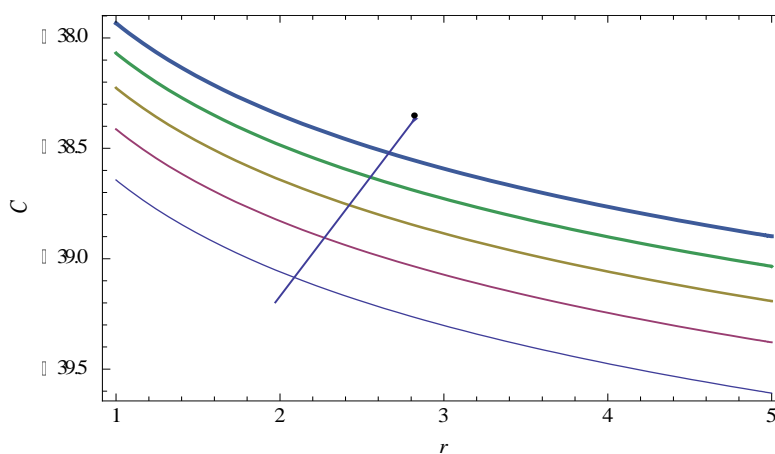
Figure 1: Dependence of Concentration on radius of diffusing entity with Temperature varying for Cu–Cu diffusion
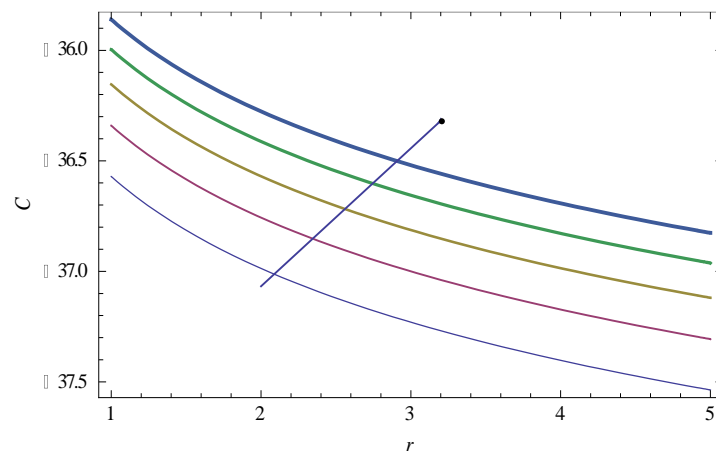
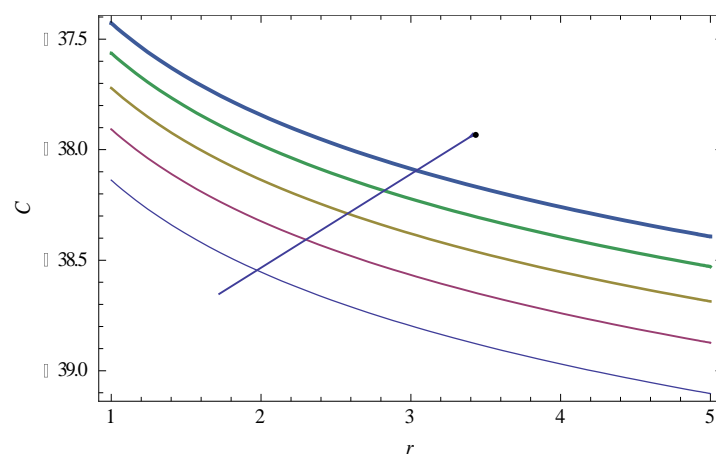**Figure 2** :Dependence of Concentration on radius of diffusing entity with Temperature varying for Zn – Cu diffusion

Figure 3: Dependence of Concentration on radius of diffusing entity with Temperature varying for Al – Al diffusion
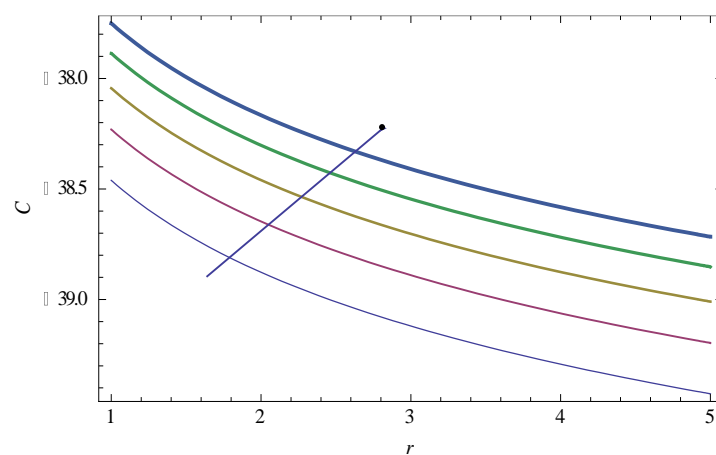

Figure 4: Dependence of Concentration on radius of diffusing entity with Temperature varying for Cu – Al diffusion
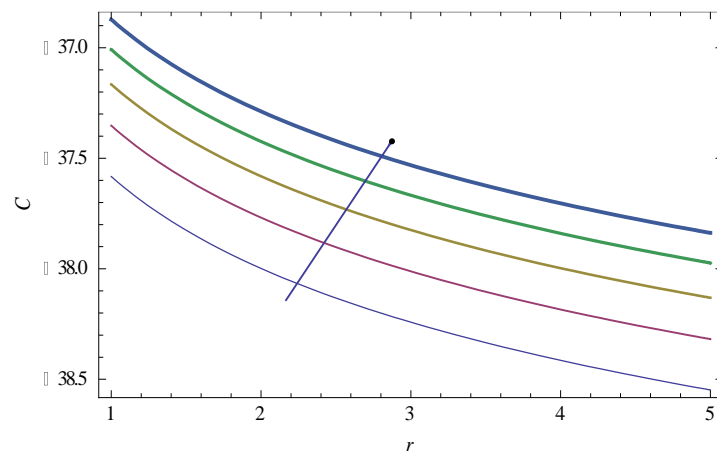
Figure 5: Dependence of Concentration on radius of diffusing entity with Temperature varying for Cu − Ni diffusion
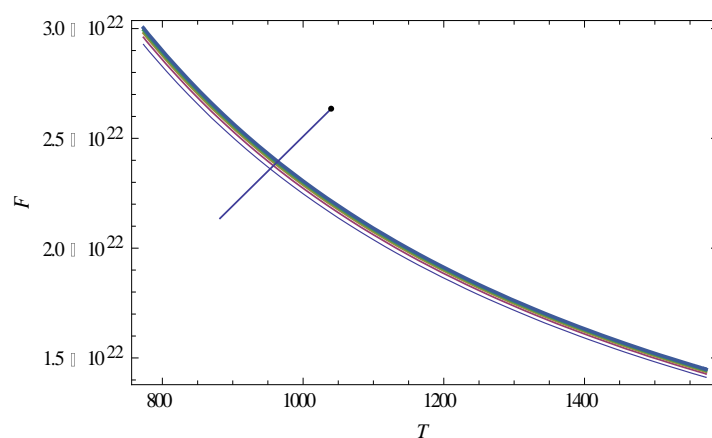

Figure 6: Dependence of Helmholtz Free Energy on Temperature with radius of diffusing entity varying for Cu–Ni diffusion
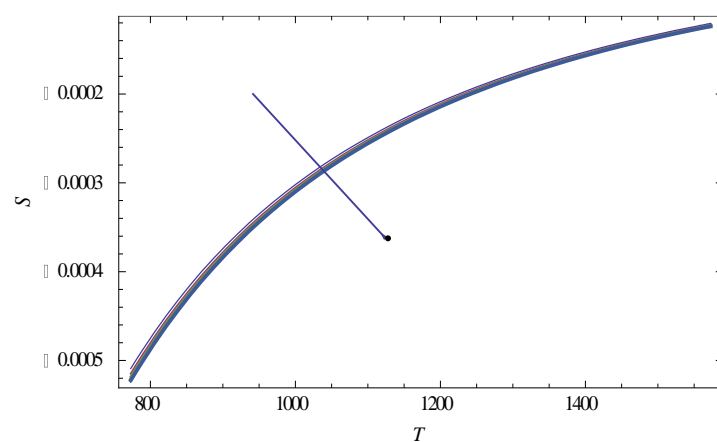

Figure 7: Dependence of Entropy on Temperature with radius of diffusing entity varying for Cu–Ni diffusion
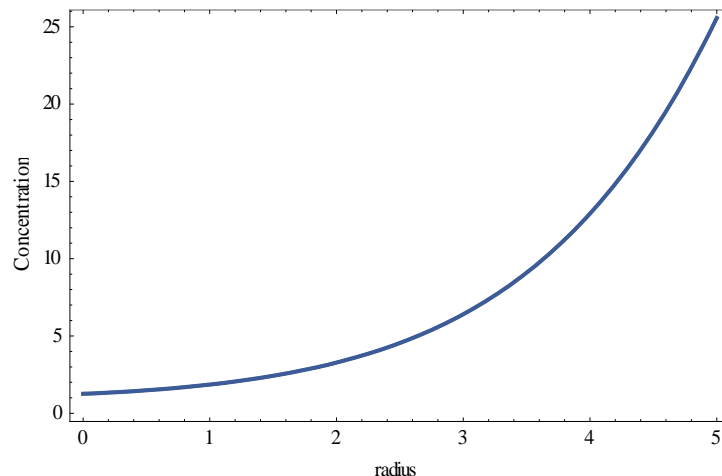
Figure 8: Dependence of Concentration on radius of diffusing entity with Temperature varying for Cu–Cu diffusion

4. DISCUSSION

Equation (14) and Figures (1-5), depict the behaviour of concentration of diffusing species on temperature. It is shown that increase in temperature of the diffusing species result in a corresponding increase in the concentration. This observation indicates that increase in temperature, provide higher diffusion coefficients because the atoms have higher thermal energies and therefore higher certainty of being activated over the energy barrier between the atoms. This observation is in agreement with the work of Rajput (2003). Tables 1 and 2 also show that the values of diffusion coefficient obtained from our study fits well with that of experimental data. Equation (18) gives an expression for the partition function which described the thermodynamic properties of the diffusing species and host metals of the system. The equation showed that increase the radius of diffusing species at a fractional exponent of 0.6 within the temperature range of 773k – 1573k, the partition function appears to be stable in Cu-Cu diffusion, Zn-Cu diffusion, Al-Al diffusion, Cu-Al diffusion and Cu-Ni diffusion. The stability is associated with the high Avogadro's number. Figure (6) was modeled from equation (19). It is observed that increase in the radius of the diffusing specie at 0.6 exponent enhanced the Helmholtz free energy of the Cu-Cu diffusion. The same condition is observed with the Zn-Cu diffusion, Al-Al diffusion, Cu-Al diffusion and Cu-Ni diffusion. Figure (7) is the graph of equation (20). It depicts the dependence of the entropy on the temperature of the diffusing specie. An increase in the radius of the diffusing specie diminished the rate of disorderliness of the system. This observation is the same with the other diffusing species and host metals. Equations (21) and (22) respectively give an expression of the internal energy and specific heat at constant volume of the systems under consideration. The equations show that these thermodynamic functions are dependent on the temperature but independent of the pre-exponential factors, viscosities of the diffusing species and radius of the diffusing species. The simple explanation is that the internal energy and specific heat are not affected by the mentioned properties of the diffusing species. Equation (13) and graph (8) explained the relationship between the concentration of the systems and radius of the diffusing specie. A stable concentration of the system is achieved as the temperature increases. Although, the constant factor β characterize the different diffusing species and host metals in magnitude, the overall observation as the temperature increases for all the solid metals under consideration is stability after the initial increase in the concentration of the systems. A mathematical model for determining the constant diffusion coefficients for the solid metals under consideration is proposed. Analysis showed that the constant β_1 varies from the different diffusion species and host metals shown on Table 2. The value of the concentration for a given diffusion specie is obtained from equation (14), substitute into equation (3) with the appropriate constant β_1, the diffusion coefficient for the diffusing specie and host metal under consideration can be obtained.

5. CONCLUSION

The study examined an analytical method in the consideration of the diffusing species into host metals in cylindrical coordinate. The plank of the study is to lay credence to the assertion that the fractional -Stokes-Einstein equation is a better approximation to the Stokes-Einstein equation in the determination of diffusion coefficients of solids. Results obtained in the study and in particular the model proposed is in reasonable agreement with most of the literatures cited and fits experimental data.

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